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(54) Title: METHOD FOR THE PRODUCTION OF DUAL-LAYER SLAB OR BOARD-LIKE ARTICLES AND SLAB OR BOARD-LIKE ARTICLES WHICH CAN BE OBTAINED BY THE METHOD

(57) Abstract: "Bretonstone" technology is used for the production of a dual-layer slab or board-like article. The rear layer is formed from a mix comprising an inorganic granular material in expanded form, in particular consisting of beads of expanded glass, expanded day and the like, a filler in the form of a fine powder, preferably cristobalite, and a hardening resin, in particular epoxy resin or polyester. The first layer, which is intended to form the visible side of the article, comprises the same resin or a resin compatible with that present in said rear layer. A web of continuous glass filaments is arranged between the said two layers. The invention also relates to the article or slab which can be obtained by the abovementioned method.

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"Method for the production of dual-layer slab or board-like articles and slab or board-like articles which can be obtained by the method"

* * *

Description

The present invention relates to the manufacture of conglomerate slabs and more particularly to the manufacture of thin slabs or boards which have a particularly low weight, while retaining good mechanical properties.

Relatively recently a technology for the manufacture of conglomerate slabs, referred to overall as "Bretonstone" technology, has been proposed and implemented on an industrial level. This technology consists essentially in the preparation of a mix comprising granules of one or more natural stone materials or equivalent artificial materials and a binder, chosen from among natural cement binders and synthetic resins.

This mix is deposited on either a temporary support or inside a tray-like mould and subjected to a vacuum compaction step, with the simultaneous application of a vibrating movement. The resultant compacted rough slab is then subjected to a setting step, the mode of implementation of which depends on the nature of the binder. In the case of a cement binder, there will be a first setting step followed by a full setting step which lasts a few days.

In the case, however, of a synthetic resin based binder, such as for example a polyester resin or an epoxy resin, the setting step may be performed in a very short time, by heating the rough slab, if necessary with the aid of a catalyst.

The nature of the granular material forming the mix obviously affects the physical, mechanical and aesthetic characteristics of the resultant slab.

If, for example, a granular material formed by particles of granite or marble is chosen, this will provide the visible surface of the slab with particular special aesthetic properties.

Moreover, the resultant slab may be made with lower thicknesses than a slab made of the same natural stone material, at least maintaining and very often improving the mechanical properties.

Moreover, many measures have been introduced into this technology in order to improve the mechanical properties and obtain slabs with an increasingly lower

thickness.

Considering the case of conglomerate articles where the binder is a synthetic resin, it is easily understood that the weight of the slab depends practically entirely on the stone material granular material which is used.

5 In the past it was proposed to use granular material formed by light material, such as expanded clay or blown glass or similar materials.

By way of example the US patent No. 6,177,179 shall be mentioned, disclosing the production of boards, e. g. to be used as kitchen worktops, which comprise two layers, i.e. a first layer intended to form the visible surface of the board and a second
10 layer forming instead the rear side of said board.

According to the description of this patent, the rear layer or second layer of the board is made from a mixture of a resin and a granular material having a specific weight of less than 0.6 g/cm^3 chosen in particular from hollow glass beads, expanded clay, expanded glass, expanded powdered stone, pumice sand, ceramic hollow beads
15 or expanded metal.

The visible or first layer instead consists of a resin mixed with a granular material of a mineral nature.

According to the description of the patent in question, the two layers are formed by means of casting, filling a mould first with the components of the layer
20 intended to form the visible side of the article and then with those of the rear layer.

More specifically the first layer is formed by casting inside the mould a mixture consisting of a syrup of a monomer chosen from among those useful for forming acrylic, polyester or epoxy resins, with the addition of a pre-polymer compatible with the monomer and expedient in particular in the case of acrylic resins, the mixture also
25 comprising the granular material which must have a higher specific weight than the syrup with which it is mixed.

During casting of the first layer, care is taken to settle the granular material prior to the hardening of the resin so as to ensure the uniformity of distribution on the surface and consequently improve the aesthetic properties. This however results
30 in a certain lack of uniformity in the first layer.

During the real manufacture of a board according to this prior patent, before casting the second layer, a separating layer, consisting for example of a film of plastic material, is arranged on the surface of the first layer soon after it has been cast. In this

manner it is prevented that, after casting of the second layer, a movement of monomer takes place towards the second layer with a possible formation of bubbles in the first layer.

Preferably the separating layer must be able to form chemical bonds with the adjacent layers. Even more preferably, the separating layer consists of a sheet or film of plastic material, for example polypropylene, polyethylene or polyester, which preferably comprises on the surface facing the second or rear layer a protective layer consisting, for example, of a woven fabric or a glass fibre matting.

The second or rear layer is also formed by a syrup which may have, and preferably has, the same composition as the first layer.

It is also pointed out that, during the manufacturing process, hardening of the resins forming the two cast layers starts from the layer intended to form the visible side.

According to the description of the patent, the resultant article is of a light weight.

However, this technology poses not negligible problems and drawbacks from an industrial point of view.

Firstly, the casting technique requires that the mixtures are highly fluid, so that the proportion of syrup, and consequently of the monomer and pre-polymer added, is very high compared to the content of granular material. Consequently, the article has a high cost, since the resin is undoubtedly the most expensive component of the mixtures.

Secondly, the article has a considerable lack of homogeneity due, on the one hand, to settling of the granular material forming the first layer and, on the other hand, to the provision of the separating film or sheet.

Finally, one must not overlook the fact that the production by means of casting always results in very poor physical/mechanical characteristics and a limited propensity for polishing of the articles due to the required high proportion of resin compared to the content of granular material content which precludes the use of a large quantity of fine filler because it would thicken the resin excessively, therefore resulting in process difficulties.

Within the context of "Bretonstone" technology, however, articles have already been produced where the granular material in the starting mix consists of a

light material such as expanded clay.

The main object of the present invention is to provide a thin and light dual-layer article which is devoid of the problems and drawbacks mentioned briefly above and associated with the articles produced according to the known art, in particular according to the US patent No. 6,177,179.

This and other objects are achieved by a method for the production of dual-layer slabs comprising a first thin layer, preferably has a thickness of between 4.0 and 5.0 mm, of conglomerate formed from a mix comprising a granular material, a filler and a hardening resin, in which the granular material is intended to form the visible side of the final slab article and determine its aesthetic properties, and a second layer, or thicker rear layer, preferably having a thickness of between 2.0 and 4.0 cm, formed from a mix comprising a hardening resin which is identical to or compatible with that forming said first layer, a filler and a granular material made of light material, said method comprising the following steps:

(a) preparation of a mix consisting of a hardening resin, a filler and a granular material intended to form the visible side of the final slab article;

(b) deposition of the mix in the form of a thin layer - referred to below as first layer - on a support consisting of rubber or similar elastic material - or first rubber sheet - lined with a separating material;

(c) deposition, on the free surface of said first layer, of a web of continuous glass filaments pre-impregnated with a hardening resin identical to or compatible with that forming the mix of said first layer;

(d) deposition, on top of said web, of a thicker layer - referred to below as first layer - of a mix formed by a hardening resin having a nature identical to or compatible with that present in said first layer and in a quantity substantially equal thereto, by a filler and by a light granular material;

(e) application, on top of the free surface of said second layer, of a second sheet of rubber or elastic material lined with separating material;

(f) vacuum compaction by means of application of a pressure on top of said second slab and of a vibratory movement of predetermined frequency;

(g) setting of the hardening resin by means of the action of heat and/or a catalyst;

(h) finishing of the resultant slab article,

wherein a filler in the form of a fine powder is added to said mixes.

In the preferred embodiment of the method according to the present invention, said light granular material present in the mix of said second layer is an expanded inorganic material with a substantially spheroidal form and having a grain size of between 0.1 and 6.0 mm, chosen preferably from expanded glass or expanded clay, without however excluding the use of other expanded inorganic materials such as alumina.

As a hardening resin, an epoxy resin or a polyester resin is preferably used; in this second case, in a manner known in the art, an organofunctional silane - having the function of forming a chemical bond between the resin and the silicon atoms in the granular material of the mix - is added to the resin.

As regards the granular material present in said first layer, i.e. that intended to form the visible side of the resultant slab or board-like article, it is chosen from among those normally used in "Bretonstone" technology, namely natural stone materials (marble, granite, porphyry, quartz, etc.) and man-made materials such as ceramic materials.

In said first layer, when particular decorative effects are required, it is possible to add other materials or components, such as metal elements, shells, metallized glass granules, fragments of a mirror, silicon granules, etc.

Finally, considering now the filler, it forms, together with the resin, the binding matrix which encapsulates and retains the granular material. The filler is chosen preferably from quartz or carbonate powders, with preference for cristobalite in powder form when it is required to obtain a lighter article. In fact, cristobalite is an allotropic form of quartz with a specific weight of 2.30, while quartz has a specific weight of 2.65.

During the setting step of the method according to the present invention, performed, as already mentioned, by means of catalysis accompanied by heating of the rough-finished article resulting from the vacuum vibro-compaction step, the two sides of the rough-finished article, still enclosed by the rubber slabs, are positioned in contact with two heating plates.

As already mentioned, the two aforementioned layers contain either the same hardening resin or resins compatible with each other in substantially equal quantities, in order to avoid varying shrinkage or warping during catalytic hardening and to also

have the same thermal expansion coefficient, so that a deformation of the article once installed, following temperature fluctuations, is avoided. There exists, however, a difference in composition between the two layers which could have similar consequences if steps were not taken to compensate for this imbalance. In particular, the thicker light layer containing granules of expanded material, has a lower heat transmission coefficient which causes it heats more slowly. In order to compensate for this lower heat conductivity, the heating surface in contact with said light layer must be warmer.

For this reason, during hot catalysis, a temperature gradient is established between the two surfaces in contact with the two sides of the rough-finished article, so as to bring the surface which performs heating of said second layer to a temperature which is 6 to 15 °C higher than the surface in contact with the rubber slab which covers the outer side of said first layer. In this way, the lesser heat conductivity of the said second layer is compensated for and the speed of heating of the two layers of the rough-finished article is made uniform, eliminating another possible cause of deformation of the resultant slab or board.

Finally, as regards the web of glass fibres impregnated with hardening resin, its characteristics and its function in the context of Bretonstone technology have been illustrated in the patent application No. PCT/EP2004/008242 to which reference should be made for further details. In this new product the web also performs the function of keeping the two mixes separate, preventing the light layer from being able to contaminate the visible layer, which must maintain optimum aesthetic features.

By the method according to the present invention a slab or board-like article with the required properties of lightness and a low overall thickness is obtained, wherein said first layer forming the visible side has a thickness of between about 4 and 6 mm, while said second layer has a thickness in the range of about 10 to 40 mm.

During the production of articles according to the invention and in particular the layer forming the visible side, it is possible to use measures which are already known in "Bretonstone" technology, in particular as regards colouring of the mixes and the creation of special chromatic and/or aesthetic effects.

Moreover, with the method according to the present invention, the resultant slab or board-like article has mechanical properties comparable to those of a slab

obtained using "Bretonstone" technology, therefore retaining the advantages which form the basis of the commercial and industrial success of the "Bretonstone" technology.

For a better understanding of the invention, an example of embodiment, based on the compositions of the mixes forming the two layers, is now provided.

Example

A single polyester resin has been used in the two mixes indicated below.

Composition (% by volume) of the visible thin layer:

- Polyester resin: 18%
- Fine quartz dust: 22%
- Quartz granular material, 0.1 – 2.5 mm 60%

Composition (% by volume) of the light thick layer :

- Polyester resin: 18%
- Fine cristobalite powder: 18%
- Expanded glass in granules of 0.2–4.0 mm : 64%

The mix of the first layer (visible side) was divided and coloured in three parts, one of which black and the other two using a coloured paste, so as to make full use of the transparency properties of quartz.

The first mix (visible side) was deposited on a rubber sheet having a thickness of about 4 mm and reinforced with a glass meshwork, performing the deposition through a sieve of 8 mm thickness having meshes of 50 x 50 mm.

A web of continuous glass filament having a weight of 300 g/m² and impregnated with polyester resin in an amount of 300 g/m² was deposited on the first mix layer.

After screening the second mix (i.e. that containing the expanded glass granular material) a second rubber sheet was applied and a vacuum pressing performed at a pressure of a few bars, applying at the same time a vibratory movement with a frequency of between 2,000 and 4,000 Hertz. At last, the resultant rough-finished article was subjected to the catalytic setting step at a temperature of between 80 and 150°C.

A perfectly flat slab was thus obtained with dimensions of 3 x 1.4 m, an overall thickness of 35 mm, a flexural strength of 135 kg/cm² and weight of 41 kg/m².

From the above description it is clear that the objects indicated above are achieved by the present invention.

In particular, a slab or board-like article is obtained which is suitable for the realization of floors and claddings, both inside and outside a building, such an article
5 possessing, in addition to the characteristic features of the already known "Bretonstone" slabs, a reduced weight of more than 50%.

It is important to emphasize that in the present invention these objects are achieved owing to the combined use of vacuum vibro-compaction, which is characteristic of Bretonstone technology, of the intermediate web of continuous glass
10 filaments impregnated with hardening resin, and the filler which forms the binding matrix together with the resin.

It is also understood that all the improvements developed in the past in connection with the "Bretonstone" technology, both in a plant where the articles are manufactured and in the structure of the said articles, may be used in the method of
15 the present invention.

* * *

Claims

1. Method for the production of dual-layer slabs comprising a first layer of conglomerate formed from a mix comprising a granular material, a filler and a hardening resin and a second layer, or rear layer, formed from a mix comprising a hardening resin which is identical to, or compatible with, that forming said first layer, and a granular material of a light weight, which comprises the following steps:

(a) preparation of a mix consisting of a hardening resin and a granular material intended to form the visible side of the final slab article;

(b) deposition of the mix in the form of a thin layer - referred to below as first layer - on a support consisting of rubber or similar elastic material - or first rubber sheet - lined with a separating material;

(c) deposition, on the free surface of the first layer, of a web of continuous glass filaments pre-impregnated with a hardening resin identical to, or compatible with, that forming the mix of said first layer;

(d) deposition, on top of said web, of a layer, - referred to below as second layer - of a mix formed by a hardening resin having a nature identical to, or compatible with, that present in said first layer, by a filler and by a light granular material, the said hardening resin being present in the mix with a volumetric percentage substantially equal to that present in said first layer;

(e) application, on top of the free surface of said second layer, of a second sheet of rubber or elastic material lined with separating material;

(f) vacuum compaction by means of application of a pressure on top of said second rubber sheet and simultaneous application of a vibratory movement of predetermined frequency;

(g) hardening of the hardening resin by means of the action of heat and/or a catalyst;

(h) finishing of the resultant slab article;

wherein a filler in the form of a fine powder is added to said mixes.

2. Method according to Claim 1, characterized in that said light granular material present in the mix of said second layer is an expanded inorganic material with a substantially spheroidal form, the granules having a size of between 0.1 and 6.0 mm.

3. Method according to Claim 2, characterized in that said light granular material is chosen from expanded glass, expanded clay or other expanded inorganic

materials such as alumina.

4. Method according to Claim 1, characterized in that said hardening resin is preferably an epoxy resin or a polyester resin.

5 5. Method according to Claim 4, characterized in that an organofunctional silane is added to the polyester resin.

10 6. Method according to Claim 1, characterized in that said granular material present in said first layer, intended to form the visible side of the resultant slab or board article, is chosen from natural stone materials such as marble, granite, porphyry, quartz, etc. and man-made materials such as ceramic materials or other materials of lithoid appearance, such as glass, silicon, shells, metals, etc.

7. Method according to Claim 1, characterized in that said filler is chosen from quartz or carbonate powders.

8. Method according to Claim 7, characterized in that said quartz is in the form of powdered cristobalite.

15 9. Dual-layer slab article obtained by the method according to any of the preceding claims.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 786 325 A (TONCELLI MARCELLO) 30 July 1997 (1997-07-30) column 2, line 8 - line 35; claims 1-10; figures 1-4	1-9
A	GB 2 224 283 A (DALLA VALLE ROBERTO) 2 May 1990 (1990-05-02) page 1, line 10 - page 2, line 19; claims 1-15; examples 1-6	1-9
A	WO 01/45921 A (TONCELLI MARCELLO) 28 June 2001 (2001-06-28) page 1, line 8 - line 32; claims 1,16-34 page 4, line 15 - line 32 page 10, line 1 - line 31 page 11, line 4 - line 10 page 13, line 3 - line 27	1-9
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 6 177 179 B1 (GEIER JOSEF ET AL) 23 January 2001 (2001-01-23) cited in the application column 7, line 37 - column 8, line 49; claims 1-7 -----	9

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Information on patent family members

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